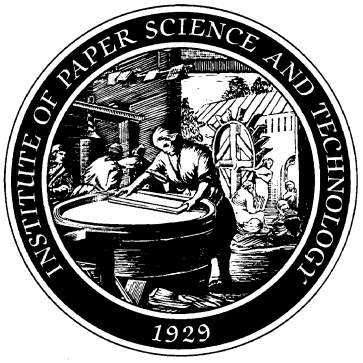

Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 675

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August 1997

Submitted to
Wood and Fiber Science

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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CONTACT ANGLE MEASUREMENT OF WOOD FIBERS IN SURFACTANT AND POLYMER SOLUTIONS

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Keywords: Contact angle, hydrophobic, wood fiber, wettability, surfactant, polymer, adsortion.

ABSTRACT

The Wilhelmy principle was used to investigate the wettability of wood fibers in various aqueous solutions. The sensitivity and reproducibility of the measurement were significantly improved by using a group of separated fibers as compared to a single-fiber method that was reported previously. This accurate and reproducible method allowed us to investigate contact angle and wettability of wood fibers in aqueous solutions using common dynamic contact angle equipment without the interference of capillary and roughness from the paper sheet surface.

The wettability of different solutions on various wood fibers, including bleached and unbleached, and AKD (alkyl ketene dimer) sized and unsized fibers, was studied. The results indicated that the receding contact angle of aqueous solution against wood fibers is zero or close to zero regardless of the nature of the wood fiber surface. However, the advancing contact angle of aqueous solution against wood fibers strongly depends on the fiber surface properties.

A decrease in advancing contact angle with an increase of the surfactant concentration was observed for all types of surfactants and fibers used in this study. The water-soluble cationic polyDADMAC [poly(dially dimethylammonium chloride)] and anionic PEO (polyethylene oxide) have no significant effect on the wettability of wood fibers in aqueous solutions.

INTRODUCTION

The contact angle of aqueous solutions on a wood fiber surface is very important for papermaking, paper printing, and recycling. However, the methods that can be used for contact angle measurement of small wood fibers in liquid are limited. The results obtained from wettability measurement by using a paper sheet may lead to a misunderstanding because of the interference of porous structure and surface roughness of a paper sheet. It is important for papermakers to know the surface properties of individual fibers rather than that of paper sheets in some cases because the fibers in pulp suspension are separately suspended in water. The surface chemistry of the individual fibers is also important for paper recycling industry. For example, the fiber-ink and fiber-air bubble interactions in a flotation deiniking cell will strongly depend on the surface chemistry of individual fibers.

It has been well-known that the adsorption and orientation of surfactant or polymer molecules on the matrixes will significantly affect the hydrophobicity of a solid surface. In a recent study of fiber fractionation by using a flotation technique, it has been found **[1,2]** that long fibers float easier than pulp fines. To explain this phenomenon, Li and Muvundamina **[1]** assume that surfactant molecules have different orientations on fines and fibers. The surface of fines is more hydrophobic than long fibers because of its high lignin content. When surfactants adsorb on fines, the hydrophobic tails of surfactant anchor onto hydrophobic sites of fines and leave the charged heads (or hydrophilic parts) toward the water phase. This leads to an increase of hydrophilicity of the surface of fines and prevents them from adhering onto air bubble surfaces. For long fibers, on the other hand, the surface is very hydrophilic, and surfactant adsorption is through the interaction

between hydroxyl groups of fiber surface and charged heads of surfactant molecules (or hydrophilic parts of nonionic surfactant). However, no direct contact angle data support this assumption.

It is difficult to measure the contact angle of liquid on individual wood fibers because the fiber length is too small to be handled, and the wetting force of a single fiber in solution is too small to be measured. The optical measurements of contact angles of liquids against fibers have been attempted by Foote **[3]**, Jones and Porter **[4]**, and Grindstaff **[5]**. However, the reproducibility of these methods is poor because it is difficult to accurately measure the contact angle of liquid on very small wood fibers using an optical technique. Furthermore, these methods yield only a single θ-value, which may be highly unrepresentative of the average properties of the heterogeneous fiber. A more satisfactory approach to the determination of fiber-liquid contact angles employs the Wilhelmy principle, in which the downward force upon a single fiber suspended vertically through the liquid surface is measured **[6-8]**. However, a poor reproducibility was observed when a single fiber was used because (1) the heterogeneity of wood fibers is high and the data obtained using a single fiber may be significantly different from the average value of a pulp furnish, and (2) the wetting force is too small, which results in a large uncertainty. Instead of using a single fiber, a technique using a group of separated fibers has been developed in this study, and the wettability of wood fibers in different aqueous solutions has been studied.

EXPERIMENTAL

Surface tension and contact angle measurements:

The surface tension of a liquid solution was measured by a dynamic contact angle analyzer (Cahn DCA 312) using a glass plat. The instrument used for contact angle measurement is shown schematically in **Figure 1**.

For an object immersed in a liquid, the dynamic wetting force can be written as

$$F = P\gamma\cos\theta - (\rho_l - \rho_g)V \quad (1)$$

where F is the force on the object; P is the wetted perimeter; γ is the surface tension of liquid-air surface; θ is the contact angle of liquid on a solid surface; V is the submerged volume, and ρ_l and ρ_g are the liquid and air densities, respectively.

Because the buoyancy force is negligible compared to the total force for very small fibers (about 1% of total wetting force) **[6-8]**, the dynamic wetting force reduces to

$$F = P\gamma\cos\theta \quad (2)$$

However, using **Equation (2)** to calculate the contact angle of wood fiber depends on the accurate value of the fiber perimeter. Although Young **[9]** used a light microscope equipped with a calibrated eyepiece to measure the fiber perimeter, the swelling degree of fiber in liquid, the heterogeneity of the fiber perimeter along the fiber length, and the capillary effects from fiber surface roughness and hollow structure cannot be measured

The liquid is contained in a 50-ml glass beaker that can be raised up and down by a traveling elevator system, which allows the liquid to advance or recede over the sample at controlled rate (0.01 mm $min.^{-1}$). One end of 5-7 individual fibers was separately stuck on the adhesive tape keeping the other end in a straight line (see **Figure 1**). The ends of the fibers were carefully cut to the same level, if necessary. The distance between individual fibers were greater than 1 mm to avoid the effect of capillary force between two fibers. The dynamic wetting forces on the fibers was measured by an electronic microbalance (0.1 mg resolution) and analyzed by a computer using DCA software.

Materials

The fibers used in this study are given in **Table 1**. The fiber lengths were determined by image analysis. The width of fibers was measured using 400× magnification with the aid of OPTIMAS image analysis software. The sized fibers were made by the reaction of fibers with varying amounts of a cationic AKD sizing emulsion (Hercon 70, Hercules Inc.) in ~3% fiber consistency for 5 minutes. The furnishes were filtered and air dried for 2 hours. The air-dried fibers were then heated to 100°C in a vacuum oven for ~30 minutes.

Triton X-100 (analyze grade, J.T. Backer Inc.), cetyltrimethylammonium bromide [$CH_3(CH_2)_{15}N(CH_3)_3Br$, CTMAB, Adrich, 95%], and sodium dodecylsulphate (SDS) (Specially pure, BDH Inc.) were used as nonionic, cationic, and anionic surfactants, respectively. Poly(diallyldimethylammonium chloride) (polyDADMAC, Polysciences Inc., 15% solid) was used as a water-soluble cationic polyelectrolyte. The charge density of the polymer, determined by colloid titration, was 7.075 meq/g. Polyethylene oxide (PEO,

10,000 g/mol) was used as a nonanionic polymer. All of the surfactants and polymers were used as received.

RESULTS AND DISCUSSION

The typical curves of receding and advancing dynamic wetting forces measured using a group of separated fibers are shown in **Figure 2**. During the measurement, the fibers were immersed in (advancing) or pulled out (receding) of the liquid at a constant velocity. When the fibers were immersed into the liquid, a trace of the advancing force was recorded from **A** to **B**. It was noted that the advancing wetting force obtained by a group of separated fibers increases very slowly with the immersed fiber length, which is significantly different from the trace of wetting force obtained by a glass plate in the same liquid, i.e., a sharp increase in the wetting force is usually observed when a glass plate is immersing into the liquid. Several factors may slow the increase of advancing wetting force of wood fibers. First, the fibers were gradually swelled when dry fibers immersed into an aqueous solution. Because the fiber swelling will result in an increase in the fiber perimeter, the dynamic wetting force must gradually increase. Second, the wood fibers are heterogeneous along the fiber length. The heterogeneity of the fiber perimeter along its length (needle-like shape) is easy to see under a microscope, which must result in a gradual increase in the fiber wetting force when fibers are immersed into the liquids. Furthermore, the fibers may not attach to the liquid surface simultaneously, which results in an increase in the wetting force when more fibers are immersed into the liquid.

As the fibers were immersed further from **B** to **C**, a constant advancing force was recorded. The trace of wetting force from **B** to **C** is also different from the trace of water over a glass plate. For a glass immersing into water, the wetting force decreases with submerged volume because of the increase of buoyancy force, but a constant force was obtained when wood fibers were used instead of a glass plate. It is well-known that in order to calculate a contact angle using the Wilhelmy principle, it is necessary to extrapolate the dynamic wetting force to zero-submerged volume to eliminate the buoyancy force. However, it is difficult to detect where the zero-submerged volume is if a group of separated fibers is used because all fibers may not attach to the liquid surface simultaneously. Fortunately, as discussed before, the buoyancy force obtained from a group of separated fibers may be negligible compared to the total wetting force, which suggests that it is not necessary to extrapolate the dynamic wetting force to zero contact point. This is confirmed by **Figure 2,** which shows that the wetting force is independent of the submerged volume of fibers from **B** to **C**.

Comparing the calculated buoyancy force to the total wetting force shown in **Figure 2**, it was found that the maximum buoyancy force of wood fibers in water was only ~1% of the total wetting force. This suggests that the total advancing wetting force of wood fibers in a solution can be directly obtained from **B** to **C** without any correction to the submersed volume. A similar conclusion can also be expected for the receding force. In this study, the stable dynamic wetting forces (**B** to **C** for advancing, and **D** to **E** for receding) were directly used to calculate the contact angles.

After fibers reached the maximum depth at **C**, they were gradually pulled out from the liquid until reaching position **D**, at which a stable receding force was obtained. The receding force remained constant from **D** to **E** and then decreased from **E** to **F** where the fibers were totally pulled out from the liquid.

The dependence of the total force on the wetting time was observed in this study. It can be seen from **Figure 2** that the advancing force of the first cycle is smaller than that of the second, but the receding force is the same for the first and second cycles. This is not surprising because the advancing wetting force was obtained from dry fibers for the first cycle, but from wet fibers for the second cycle. Obviously, dry fibers have different perimeter and surface properties from wet fibers. After the first cycle, the fibers were wet and both the fiber perimeter and the wetting forces reached an equilibrium value. For the receding force, the fibers were always wet regardless of whether it was the first or the second cycle. The difference in advancing contact angles between the first and the second cycles was observed for all of the fibers and the solutions, such as bleached fibers and sized fibers in TX-100 solutions, and unbleached hardwood fibers in different surfactant solutions. After fibers were wet, stable wetting forces were obtained for both advancing and receding processes. All of the measurements made in this study were reproducible with an experimental error of less than ±8%.

Verification of zero-receding contact angle

Although Klungness **[10]** and Hodgson and Berg **[6]** indicated that the receding contact angle of water over a single wood fiber is zero, further experimental proofs are needed, particularly for the sized fibers in a surfactant or polymer solution.

For the same fibers in different solutions (surfactant, polymer, etc.), **Equation (2)** gives the following relationships:

$$\frac{F_R^1}{\gamma^1} = p\cos\theta_R^1$$

$$\frac{F_R^2}{\gamma^2} = p\cos\theta_R^2$$

. . . . .

$$\frac{F_R^n}{\gamma^n} = p\cos\theta_R^n \qquad (4)$$

where the superscriptions *1*, *2*, and *n* represent the different solutions. If the zero-receding contact angle assumption can be used for the same fibers in different solutions, **Equation (4)** can be rewritten as

$$\frac{F_R^1}{\gamma^1} = \frac{F_R^2}{\gamma^2} = \cdots\cdots\cdots = \frac{F_R^n}{\gamma^n} = p \qquad (5)$$

Equation (5) indicates that, if the receding contact angle is really zero, the force ratio ($\frac{F_R^n}{\gamma^n}$) must be a constant that equals the perimeter P of the fibers. In contrast, if the receding contact angle is not zero, $\frac{F_R^n}{\gamma^n}$ must be a function of $cos\theta_R$ and surface tension γ.

Figure 3 shows the wetting forces of a group of separated fibers as a function of TX-100 concentration. It can be seen that although the surface tension of TX-100 decreases as the surfactant concentration increases up to 190 mg/L (the critical micellization concentration of TX-100), the values of $\frac{F_R^n}{\gamma^n}$ can be described well by **Equation (5)** under experimental uncertainty. This strongly suggests that although the surface chemistry of the fibers may be different in theses solutions because of the adsorption of surfactant, the receding contact angle of aqueous solutions on these wood fibers is always equal to zero. The zero-receding contact angle assumption was further verified using different types of surfactants and polymers, such as cationic surfactant (cetyltrimethylammonium bromide, CTMAB), anionic surfactant (sodium dodecyl sulfate, SDS), and cationic polymer polyDADMAC [poly(dialyldimethylammonium chloride)]. The value of $\frac{F_R^n}{\gamma^n}$ in different surfactant and polymer solutions as a function of surface tension is given in **Figure 4**. Surprisingly, the receding contact angle of bleached southern pine fibers in all aqueous solutions is zero or close to zero even though the adsorption and the orientation of different chemicals may significantly change the surface properties. The uncertainty of the receding contact angle measured in this study will be discussed later.

The perimeter of 145 ± 9 μm for a single fiber was obtained from the data shown in **Figure 3** using **Equation (5)**. This value is 1.6 times the perimeter obtained from that of image analysis (90 μm). If we note that the perimeter obtained by image analysis is based on dry fibers and the perimeter obtained from the Wilhelmy principle is based on wet fibers, the difference between these two values is not surprising. It is also suggested from this study that although the perimeter of dry fibers can be measured by several techniques, such as image analysis and electron microscopy, it cannot be applied to the Wilhelmy Equation without the correction of fiber swelling. It should also be noted that the perimeter calculated from **Equation (5)** is only an apparent perimeter because the capillary and surface roughness may also affect the total force F_R.

The receding wetting force and contact angle of 0.6% AKD sized fibers in TX-100 solution were also examined using **Equation (5)**. Because AKD is very hydrophobic, the sized fibers used in force measurements must be stiff enough to resist bending when fibers are immersed in the liquids. Furthermore, because the advancing wetting force may be very small, even negative, when highly sized fibers are used, the electronic microbalance must be sensitive enough. These limitations make the measurements more difficult and lead to a higher experimental uncertainty. However, after several repeated measurements, it was found that when a surfactant was added into the liquid both the hydrophobicity of sized fibers and the surface tension of the liquid decreased so that the fibers could be easily immersed into the liquid without bending. It was also noted that, in a pure water system, although the sizing materials significantly decrease the advancing force of fibers, they almost do not impact the receding force. This interesting behavior is shown in **Figure 5**.

The receding forces obtained from 0.6% AKD sized fibers in various TX-100 concentrations were also examined using **Equation (5)**. The results obtained from these highly sized fibers are very similar to that shown in **Figure 4**, i.e., a constant value of $\frac{F_R^n}{\gamma^n}$ was obtained for the same fiber group in different surfactant solutions. The average values of $\frac{F_R^n}{\gamma^n}$ obtained in TX-100 for 0.6% sized and unsized southern pine fibers are (132 ± 9 μm) and (145 ± 9 μm), respectively. This very small difference suggests that sizing agents may significantly change the surface chemistry of wood fibers, but they may not significantly affect the receding contact angle of wood fibers in aqueous solutions, i.e., the receding contact angle of an aqueous solution on sized fibers can also be treated as zero. This conclusion is consistent with results reported by Hodgson et al. **[6-8].** According to **Equation (2)**, the difference in the receding contact angles for unsized and sized fibers is directly related to the ratio of their receding forces

$$F_R^{sized} / F_R^{unsized} = cos\theta_R^{sized} / cos\theta_R^{unsized} \qquad (6)$$

Because $cos\theta_R^{unsized}$ =1, **Equation (6)** reduces to

$$F_R^{sized} / F_R^{unsized} = cos\theta_R^{sized} \qquad (7)$$

The values of $F_R^{sized}/F_R^{unsized}$ measured in different surfactant solutions are plotted as a function of surfactant concentration in **Figure 6**. It can be seen that all of the $F_R^{sized}/F_R^{unsized}$ values, including those obtained in pure water and in surfactant solutions, fit the unit line with an uncertainty of ± 0.12. This leads to $cos\theta_R^{sized} / cos\theta_R^{unsized}$ = 1±

0.12. If the receding contact angle of unsized fibers in water is zero ($cos\theta_R^{unsized}$=1), the above uncertainty indicates that $cos\theta_R^{sized}$ must be in the range of 0.88 to 1, which corresponds to a receding contact angle θ_R^{sized} of 0 to 23° for these sized fibers. Although this is a wide range of values, it will only give a small correction on the advancing contact angle when **Equation (3)** is used. For example, if the advancing contact angle is 60° (most sized fibers have a $\theta_A > 60°$ in water), $F_A/F_R = cos60/cos\theta_R^{sized} = 0.588/cos\theta_R^{sized}$. Because θ_R^{sized} is in the range of 0 to 23° for sized fibers, it leads to $F_A/F_R = 0.588 \pm 0.07$. Substituting this value into **Equation (3)** gives $\theta_A^{sized} = 60 \pm 5°$. This suggests that even though the receding contact angle can be in the range of 0 to 23° for highly sized fibers the uncertainty in advancing contact angle calculated from **Equation (3)** using zero-receding contact angle assumption is small.

Although the receding force ratio of $F_R^{sized}/F_R^{unsized}$ is almost equal to one in all of the solutions, the advancing force ratio $F_A^{sized}/F_A^{unsized}$ is significantly different for sized fibers in different surfactant solutions. As surfactant concentration increases, the sized fibers sharply change from hydrophobic to hydrophilic by the adsorption of surfactant onto the fiber surfaces, but the hydrophilicity of unsized fibers changes little because they are originally hydrophilic enough. This leads to a quick increase in F_A^{sized}, but a constant $F_A^{unsized}$. As a result, $F_A^{sized}/F_A^{unsized}$ is sharply increased. It can be seen from **Figure 5** that the advancing force ratio, $F_A^{sized}/F_A^{unsized}$, increases from negative (in water) to positive, and finally reaches its maximum value (= 1 at the concentration above the CMC

The effects of different surfactants and polymers on the advancing contact angle of unsized and 0.6% AKD sized southern pine fibers are shown in **Figures 8** and **9**. **Figure 8** indicates that two surfactants, TX-100 and CTMAB, significantly reduce the advancing contact angle of water on southern pine fibers, where SDS and polyDADMAC only slightly reduce it. Similar results for 0.6% AKD sized fibers can be obtained from **Figure 9**. It is believed that the decrease in the contact angle as the surfactant concentration increases is attributed to the adsorption of surfactant on the fiber and water surfaces. It has been noted that all of the surfactants will reduce the contact angle of wood fibers in aqueous solutions regardless of the type of surfactant and the original fiber surface properties.

Comparison with previous results

The relationship between wettability and surfactant orientation on the surface of wood fibers has been discussed by Li and Muvundamina **[1-2]**. They suggested that, if the fibers are hydrophilic, the hydrophilic part of a surfactant is likely to anchor onto the fiber surface leaving the hydrophobic tail toward the liquid. In contrast, if the fibers are hydrophobic, the hydrophobic part of a surfactant is likely to adsorb onto the fiber surface leaving the hydrophilic head toward the liquid. As a result, hydrophilic wood fibers may be reversed to hydrophobic or vice versa by the adsorption of surfactant. Li and Muvundamina **[1-2]** used this assumption to explain why long fibers float easier in flotation cells than fines (fines are relatively hydrophobic because of the high lignin content). However, if their assumption is true, the adsorption of surfactant molecules must result in an increase in the advancing contact for unsized fibers and a decrease in

sized. The direct measurements of the advancing contact angles of different surfactant solutions (TX-100, SDS, and CTMAB) on all of the fibers (unsized, 0.2 and 0.6% AKD sized fibers) used in this study indicate that the adsorption of surfactants can only reduce the advancing contact angle, regardless of the nature of the surfactants (nonionic, anionic, or cationic) and the fiber properties (sized and unsized southern pines and unbleached hard wood fibers).

CONCLUSIONS

Several advantages for contact angle measurement could be achieved using a group of separated wood fibers. For example, the surface structure and the roughness effects from a paper sheet can be minimized when a group of separated fibers is used. Compared to the single-fiber technique developed by Hodgson et al. **[6-8],** the total wetting force of wood fibers in a solution can be increased by using multiple wood fibers, resulting in a decrease in experimental error. Furthermore, the heterogeneity of the fiber perimeter can be averaged out by using multiple fibers simultaneously, resulting in a smooth curve and reproducible result.

The receding contact angle of individual wood fibers in aqueous solutions can be treated as zero regardless of the type of wood fibers and the chemicals dissolved in the solution. The advancing contact angle of wood fibers in aqueous solutions strongly depends on the fiber surface chemistry. The adsorption of surfactant onto the fiber surface will significantly reduce the advancing contact angle of liquid over fibers. However, the adsorption of polymer gives only a small effect on the advancing contact angle.

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Table 1. Fiber properties.

Fibers	Average length (mm)	Average perimeter (μm)	Sizing
Bleached southern pine	2.83	90	no
0.2% AKD sized bleached southern pine	2.83	90	0.2% of AKD emulsion
0.6% AKD sized bleached southern pine	2.83	90	0.6% of AKD emulsion

FIGURE CAPTIONS

Figure 1. Schematic diagram of dynamic wetting force measurement using fiber group technique; A: electronic microbalance, B: wetting liquid, C: traveling elevator system, D: fibers, and E: computer.

Figure 2. The traces of dynamic wetting forces of distilled water on a group of 5 separated fibers.

Figure 3. Surface tension γ and force ratio F_R/γ as a function of TX-100 concentration at room temperature for bleached southern pine fibers.

Figure 4. Force ratio F_R/γ as a function of chemical concentrations of nonanionic surfactant TX-100, cationic surfactant CTMAB, cationic polymer polyDADMAC, and nonionic polymer PEO. Fibers: bleached southern pine fibers.

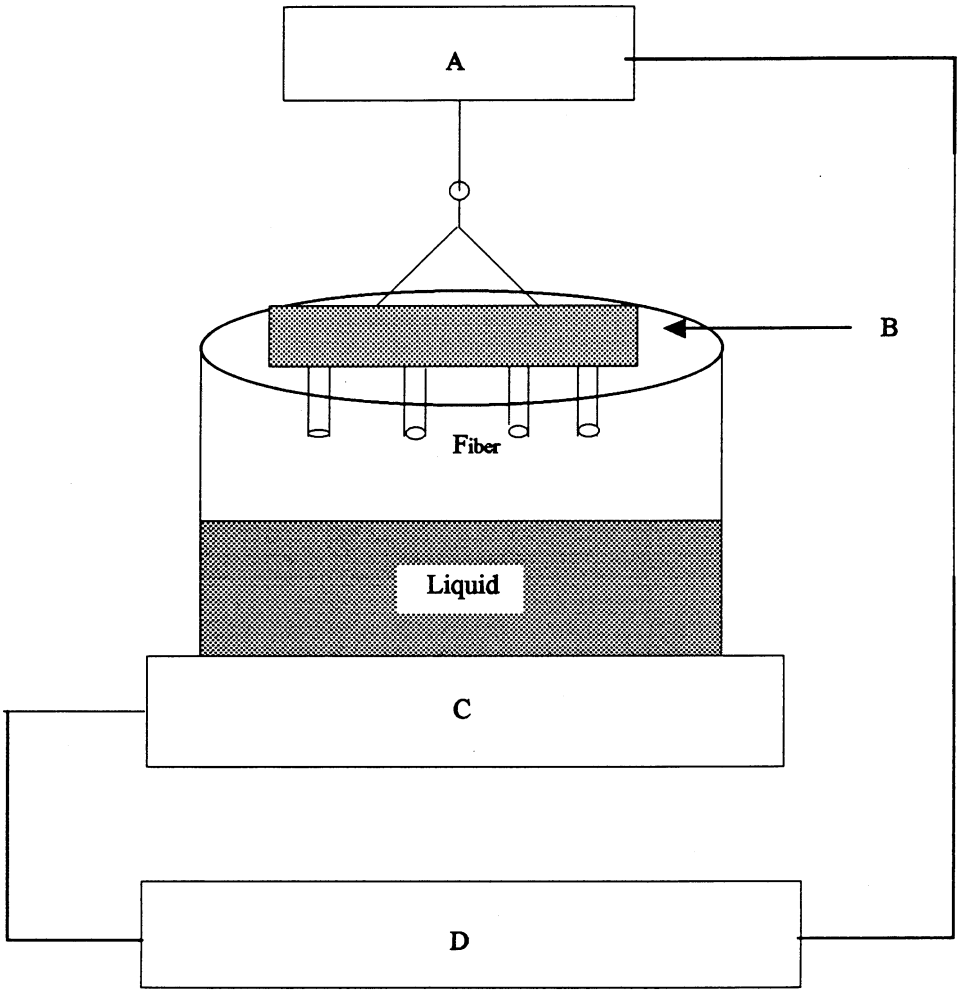
Figure 5. The traces of dynamic wetting force for 0.2% AKD sized and unsized bleached southern pine fibers in water.

Figure 6. The ratio of the dynamic wetting forces measured from unsized and 0.6% AKD sized southern pine fibers against surfactant concentration.

Figure 7. Advancing contact angle of unsized, 0.2% AKD sized, and 0.6% sized bleached southern pine fibers as a function of TX-100 concentration.

Figure 8. Advancing contact angle of unsized bleached southern pine fibers in different surfactant solutions as a function of surfactant concentration at neutral pH and room temperature.

Figure 9. Advancing contact angle of 0.6% AKD sized fibers in different surfactant solutions as a function of surfactant concentration at neutral pH and room temperature.



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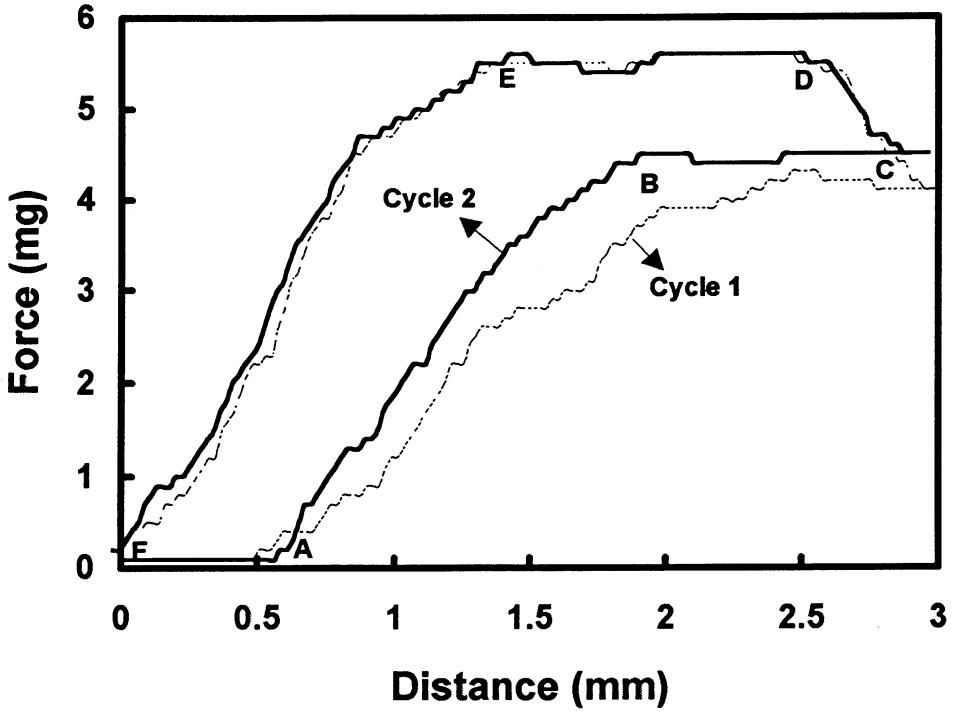

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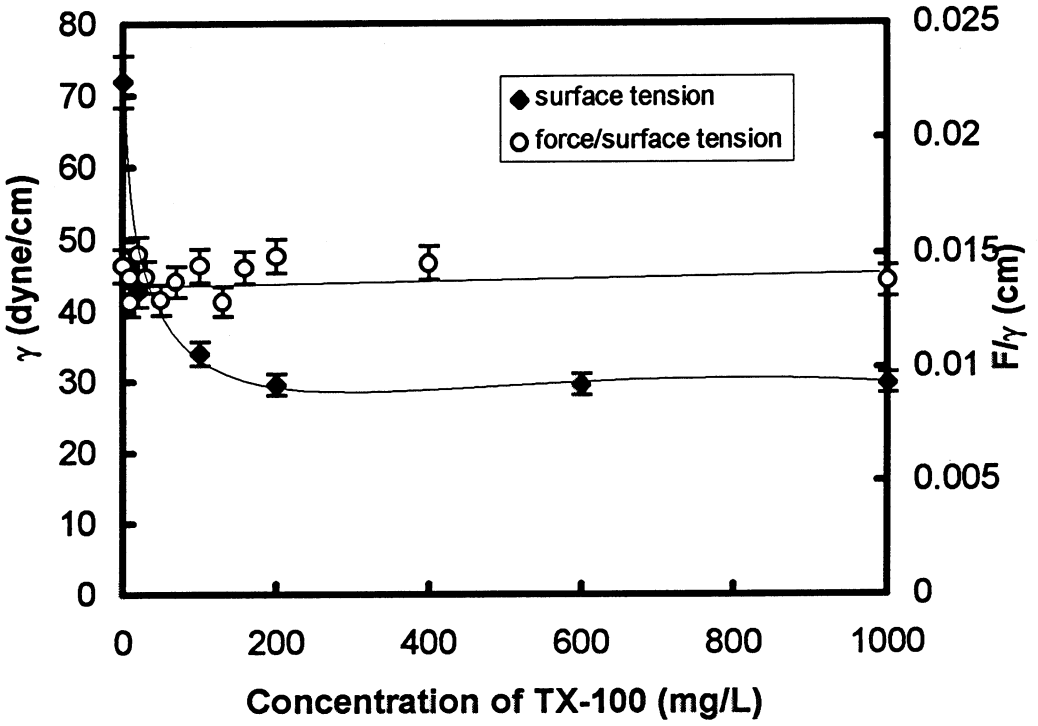

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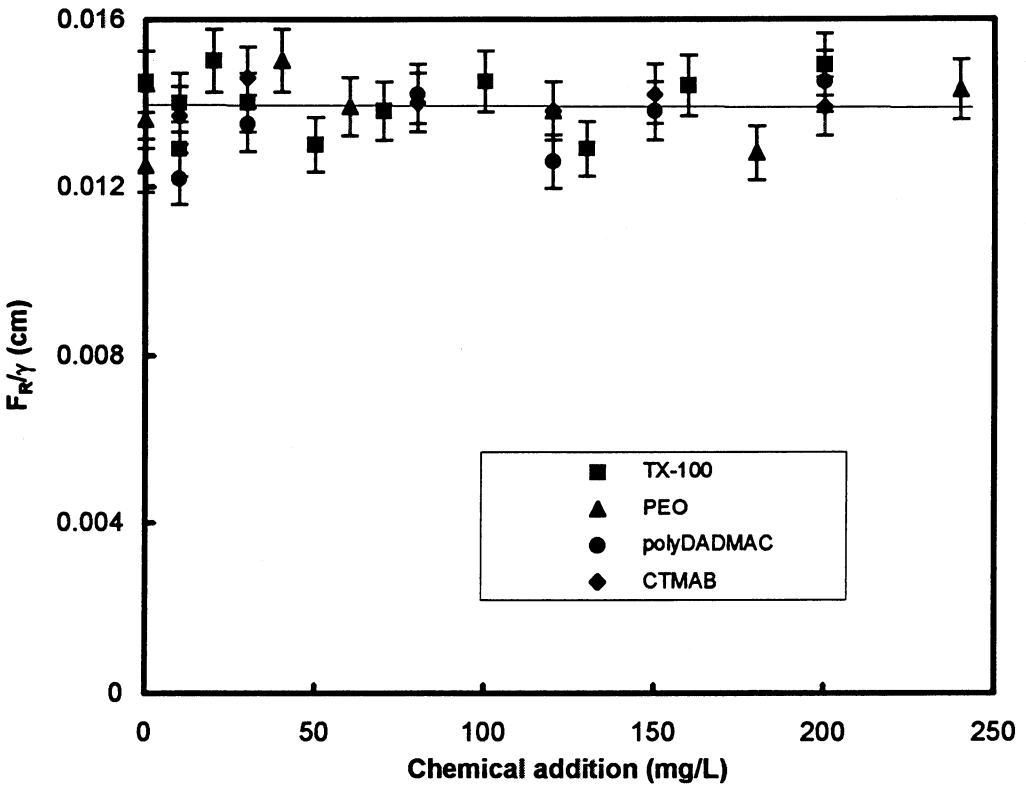

Figure 4. *Force ratio F_R/γ as a function of chemical concentrations of nonanionic surfactant TX-100, cationic surfactant CTMAB, cationic polymer polyDADMAC, and nonionic polymer PEO. Fibers: bleached southern pine fibers.*

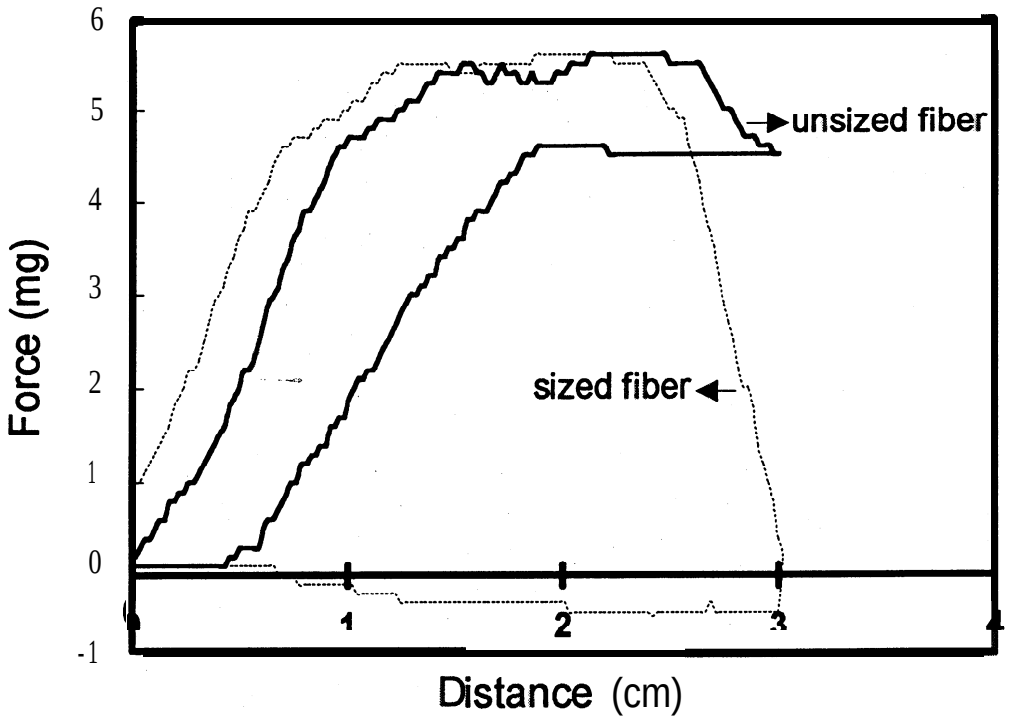

Figure 5. The traces of dynamic wetting force for 0.2% AKD sized and unsized bleached southern pine fibers in water.

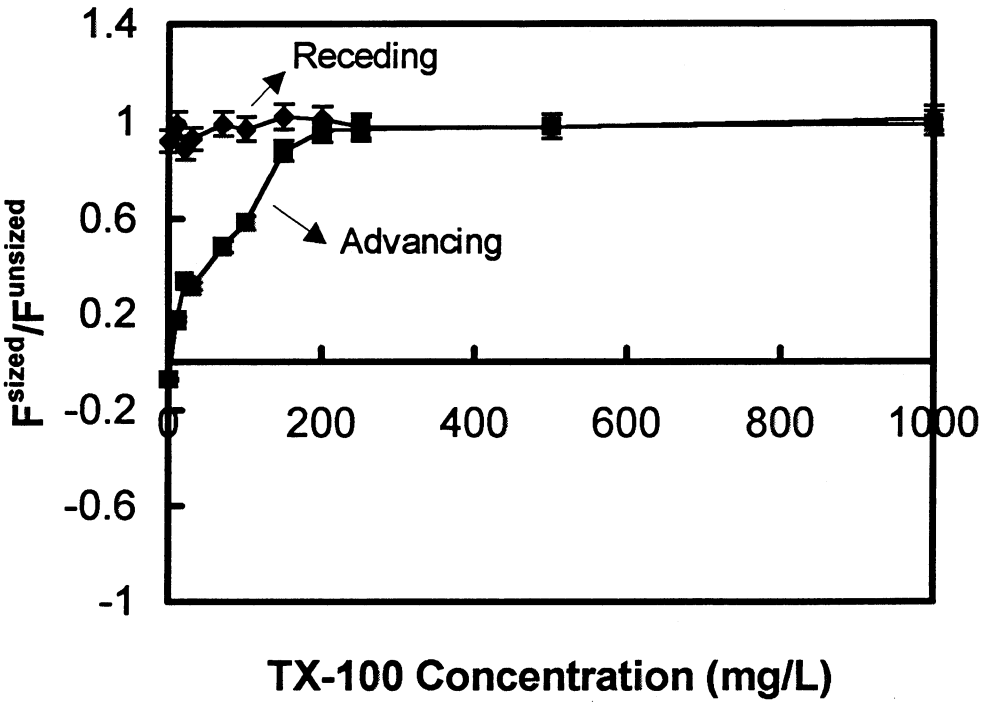

Figure 6. *The ratio of the dynamic wetting forces measured from unsized and 0.6% AKD sized southern pine fibers against surfactant concentration.*

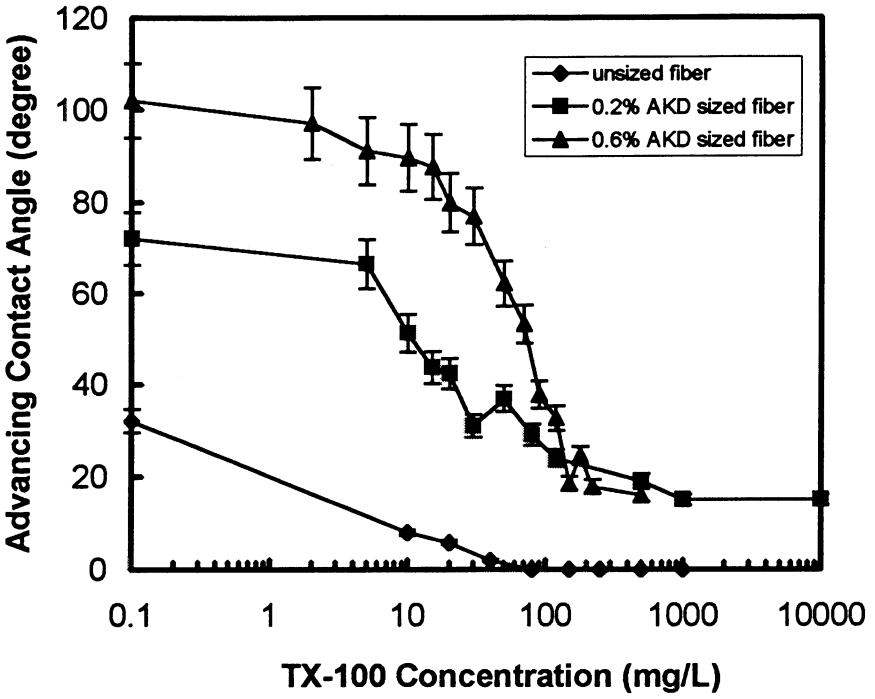

Figure 7. *Advancing contact angle of unsized, 0.2% AKD sized, and 0.6% sized bleached southern pine fibers as a function of TX-100 concentration.*

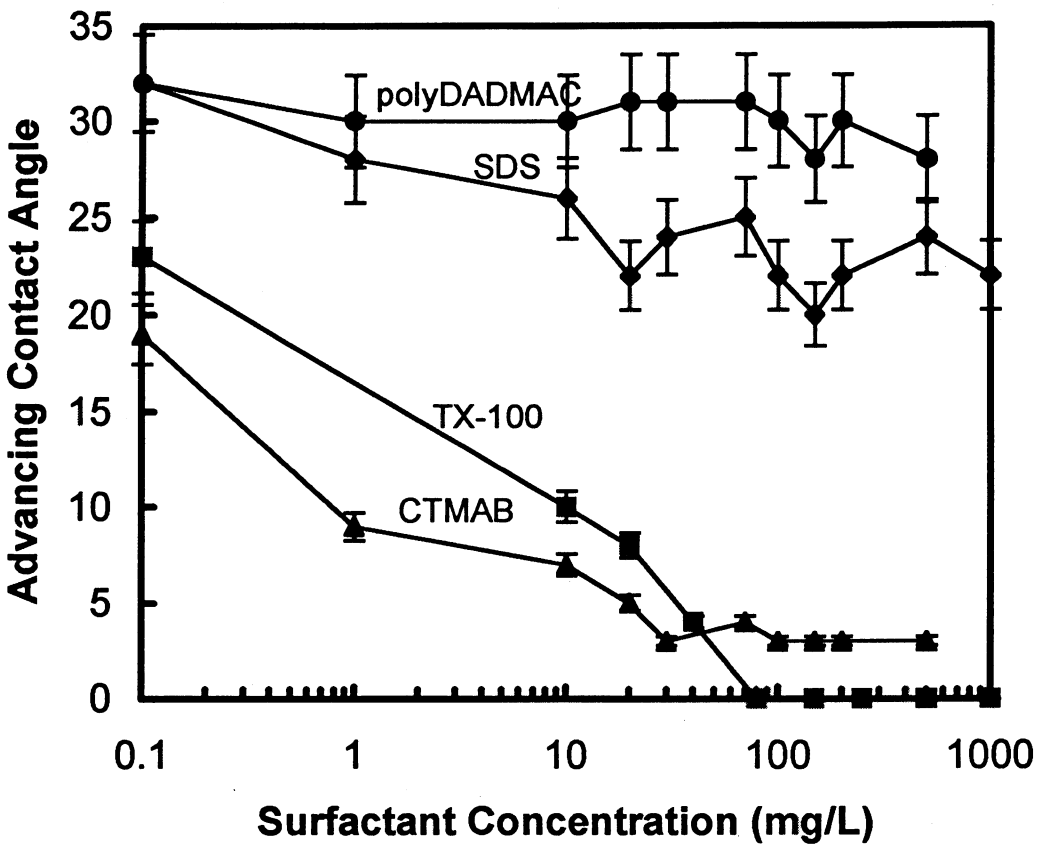

Figure 8. *Advancing contact angle of unsized bleached southern pine fibers in different surfactant solutions as a function of surfactant concentration at neutral pH and room temperature.*

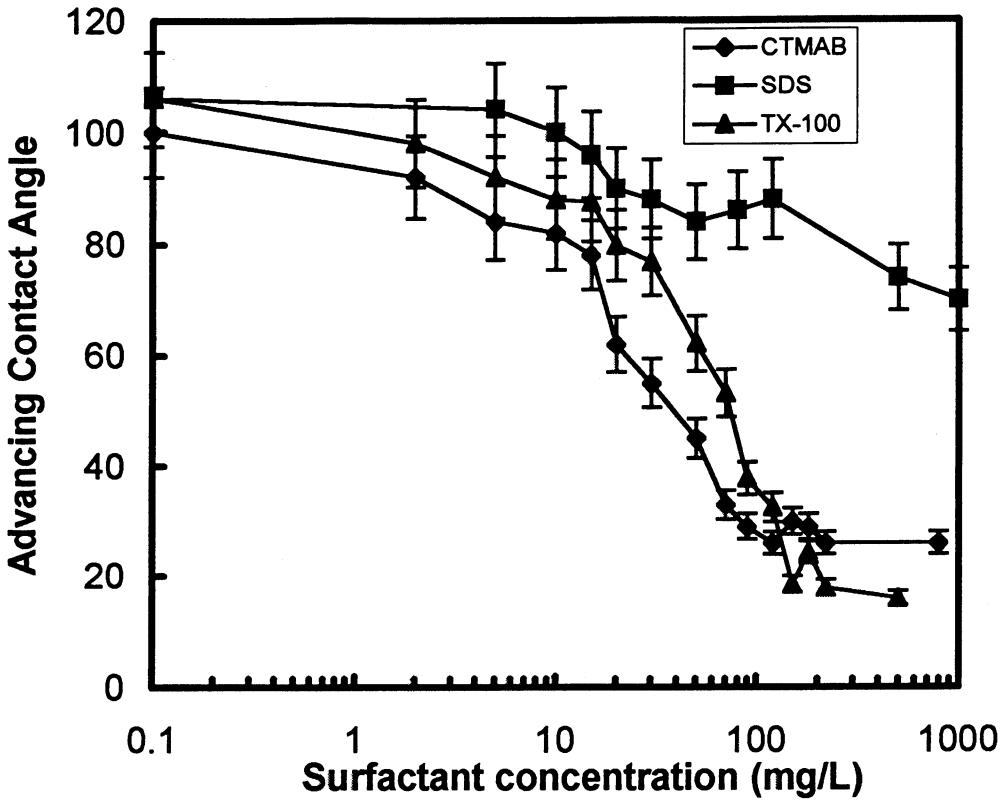

Figure 9. *Advancing contact angle of 0.6% AKD sized fibers in different surfactant solutions as a function of surfactant concentration at neutral pH and room temperature.*